



## Marked-Up Substitute Specification

### TITLE OF THE INVENTION

Mixed Conductor and Mixed Conductor Producing Method

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### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The present invention relates to a mixed conductor which exhibits both ~~electronic~~ electron conduction and proton conduction. This mixed  
10 conductor can be used for the catalyst layer of a fuel cell, a gas diffusion catalyst and the like.

#### 2. Description of the Related Art

The catalyst layer of a fuel cell is formed between a proton exchange membrane and a backing layer and supports a catalyst for accelerating an  
15 electrochemical reaction. ~~A combination of the~~ The catalyst layer ~~and the catalyst layer~~ constitutes the electrodes of the fuel cell. In the catalyst layer on an air cathode side, for example, protons passing through the proton exchange membrane and electrons transferred to the air cathode are conducted ~~[[up]]~~ to the catalyst, thus binding oxygen and protons diffused  
20 onto the catalyst. ~~Namely~~ Thus, the catalyst layer needs to exhibit both proton conduction and ~~electronic~~ electron conduction in order to ~~improve~~ reduce the transfer loss of oxygen, protons and electrons. To this end, a mixture of a poly electrolyte having catalysts supported on surfaces such as carbon particles (exhibiting ~~electronic~~ electron conduction) and Nafion  
25 (trade name, manufactured by E.I du Pont de Nemours, ~~this applies hereafter~~) which exhibits ionic conduction is used in the fuel cell.

However, if a material having ionic conduction and a material

having ~~electronic~~ electron conduction are used together, it is difficult to mix them ~~[[up]]~~ completely uniformly. As a result, protons and electrons cannot be uniformly transferred to all catalyst particles.

To solve this disadvantage, there has been proposed a mixed  
5 conductor which exhibits both ionic conduction and ~~electronic~~ electron conduction using one material.

For example, organic mixed conductors are disclosed in the following patent documents 1 to 4.

~~In addition, inorganic mixed conductors conducting electrons and  
10 oxygen ions are disclosed in the following patent documents 5 to 8.~~

Patent Document 1: Japanese Unexamined Patent Publication No.  
2001-202971

Patent Document 2: Japanese Unexamined Patent Publication No.  
2001-110428

15 Patent Document 3: Japanese Unexamined Patent Publication No.  
2003-68321

Patent Document 4: Japanese Patent Application National  
Publication (Laid-Open) No. 2002-536787

In addition, inorganic mixed conductors conducting electrons and  
20 oxygen ions are disclosed in the following patent documents 5 to 8.

Patent Document 5: Japanese Unexamined Patent Publication No.  
(10)1998-255832

Patent Document 6: Japanese Unexamined Patent Publication No.  
(11)1999-335165

25 Patent Document 7: Japanese Unexamined Patent Publication No.  
2000-251533

Patent Document 8: Japanese Unexamined Patent Publication No.

2000-18811

Since the organic mixed conductors are made of organic materials, they have many problems in terms of durability and heat resistance to be  
5 solved before being put to practical use.

As for the inorganic Inorganic mixed conductors which transfer electrons and oxygen ions[[,]] have high operating temperatures thereof are high (about 800°C). Due to this, it is considered that these inorganic mixed conductors and therefore are inappropriate for small-sized fuel cells suitably  
10 used suitable for use in, for example, vehicles and cellular phones.

## SUMMARY OF THE INVENTION

~~After exerting utmost efforts in study to solve these disadvantages, the inventor of the present invention discovered a novel inorganic mixed  
15 conductor and finally completed the present invention.~~

~~That is, the inventor of~~ In order to solve the foregoing problems, the present invention ~~discovered~~ provides a mixed conductor characterized in that in the form of an electron conductor made of an inorganic material [[is]] fixed to a proton conductor made of an inorganic material so as not to  
20 dissolve in water.

[[As the]] ~~The inorganic~~ electron conductor ~~made of an inorganic material, an electron conductor of such~~ may be a type as to cause with a main chain to have one of or both of having a carbon-carbon double bond [[and]] and/or a carbon-carbon triple bond, the main chain contributing to  
25 ~~an electronic the electron~~ conduction function as shown in Figs. 1 and 2. ~~may be used or such~~ Alternatively, the inorganic electron may be a type as to which transfer transfers electrons through a side chain.

~~It is also preferable that such an~~ The preferred inorganic electron conductor ~~uses an inorganic material~~ is obtained by carbonizing ~~[[an]]~~ at least one organic compound having a  $\pi$  bond. Examples of ~~[[the]]~~ organic compound ~~compounds~~ having a  $\pi$  bond include aliphatic hydrocarbon hydrocarbons, aromatic hydrocarbon hydrocarbons and derivatives of ~~[[the]]~~ aliphatic hydrocarbon hydrocarbons and ~~[[the]]~~ aromatic hydrocarbon hydrocarbons. ~~At least one of them is used for the organic compound having the  $\pi$  bond.~~ Typical examples of ~~[[the]]~~ such organic compounds include polyacetylene, resorcinol, phenol, phenylphenol, polyaniline, polypyrrole, polythiophene, phenylphosphonic acid, and phenylsilane alkoxide.

Further, the inorganic ~~material for the~~ electron conductor can be a carbonaceous material, such as graphite or a carbon nanotube, or a metallic material containing a metal such as gold, palladium, platinum, magnesium, lithium or titanium, or an alloy thereof.

~~As the~~ The inorganic proton conductor is made of ~~an inorganic material;~~ at least one of a phosphorus-containing compound, a sulfur-containing compound, carbonic acid, boric acid, and inorganic solid-state acid~~[[,]]~~, particularly More preferably, at least one of a phosphorus-containing compound, phosphoric acid, phosphoric ~~[[ester]]~~ acid esters, sulfuric acid, sulfuric ~~[[ester]]~~ acid esters, ~~sulfuric acid;~~ tungsten oxide hydroxide, rhenium oxide hydroxide, silicon oxide, tin oxide, zirconia oxide, tungstophosphoric acid, and tungstosilicic acid ~~can be used~~.

According to the present invention, the inorganic electron conductor and the inorganic proton conductor are fixed to each other so as not to dissolve in water. They may be fixed by ~~[[a]]~~ covalent ~~[[bond]]~~ bonding, intercalation or inclusion. However, depending on production process conditions, these ~~manners~~ types of fixing may possibly be ~~mixed~~ combined.

Further, ~~whether the state of fixing is by~~ choice of covalent ~~[[bond]]~~ bonding, intercalation or inclusion is ~~[[set]]~~ made according to the types of the materials of the electron conductor and the proton conductor. For example, if the electron conductor is ~~made of~~ an inorganic material obtained  
 5 by carbonizing an organic material, the fixing may be ~~[[made]]~~ mainly ~~[[by~~ a]] covalent ~~[[bond]]~~ bonding. If the electron conductor is made of a ~~[[metal]]~~ metallic material and an inorganic material, ~~particularly~~ especially an oxide, is selected as ~~[[a]]~~ the material for the proton conductor, for example, the both conductors can be fixed to each other by ~~[[a]]~~ covalent ~~[[bond]]~~  
 10 bonding or inclusion.

The state in which the electron conductors and the proton conductors are fixed to each other by ~~[[a]]~~ covalent ~~[[bond]]~~ bonding is illustrated in Figs. 1 and 2. Since the electron conductors 1 or 3 and the proton conductors 2 bound by ~~[[a]]~~ covalent ~~[[bond]]~~ bonding are arranged in  
 15 close proximity, both the electron conductors and the proton conductors can contact ~~[[with]]~~ a catalyst particle (e.g., platinum) in nano order as shown ~~therein~~. Accordingly, it is possible to supply electrons and protons necessary for a catalytic reaction to the catalyst in proper quantities.

Such a mixed conductor is formed as follows.

20 First, a precursor obtained by dispersing a proton conductor ~~[[into]]~~ in a polymer of an organic compound having a  $\pi$  bond is prepared.

The precursor having a proton conductor dispersed ~~[[into]]~~ in the polymer of an organic compound, or the precursor having both a proton conductor bound to an organic compound that constitutes the electron  
 25 conductor by a covalent bond and a proton conductor separated from the former proton conductor and substantially in a dispersed state.

Further a high molecular weight precursor may be formed by polymerizing an organic compound having a  $\pi$  bond with a proton conducting material. ~~In this high polymer precursor, it is considered that carbons mainly constituting~~ It is believed that in this high molecular weight  
 5 polymer precursor the carbons of the organic compound are polymerized with one another to form an electron conducting main chain having a  $\pi$  bond and also form a covalent bond with the proton conductor, and that this proton conductor bridges the carbon main chain of the electron conductor. By ~~mixing~~ adding the proton conductor in a sufficient quantities quantity,  
 10 the distance between the proton conductors bound to the carbon main chain by covalent bonds is narrowed, and proton conduction is generated between the proton conductors. ~~According to research by the inventor, It has been~~ experimentally shown that putting the polymer precursor ~~[[in a]]~~ into solution ~~[[of]]~~ with hydrolytic cleavage at 100 to 200 for several hours  
 15 promotes ~~to form~~ formation of covalent ~~[[bond]]~~ bonds between the electron conducting main chain and the proton conductor. ~~It causes improvement on~~ thereby improving proton conductivity and ~~prevention for releasing~~ preventing release of the ~~material of~~ proton conductivity conductor from the polymer precursor.

20 This precursor is subjected to pyrolysis ~~under~~ in an inert atmosphere. As a result, the organic compound is ~~carbonized~~ converted into an inorganic material by carbonization, thereby ensuring ~~electronic~~ electron conduction.

~~In addition, Because~~ the proton conductor is stably fixed to the  
 25 electron conducting carbon skeletons. ~~As a result,~~ proton conduction is ensured. It is ~~considered~~ believed that the proton conduction is attained by arranging proton conductor allocation materials ~~to be~~ conductors proximate

[[to]] each other. As shown in Figs. 1 and 2, if the proton conductors bridge the carbon skeletons, the positions of the proton conductors are fixed, thereby ensuring the proton conduction by the interaction between the proton conductors.

5           If the proton conductors are released from the carbon skeletons or if the proton conductors are not bound to the carbon skeletons from the ~~state~~ of the precursor, then ~~it is considered that~~ the proton conductors are believed to be intercalated into the carbon main chain or included in a mesh structure formed by the carbon main chain. In any case, ~~it is considered~~  
10   that the proton conduction can be ensured ~~as long as~~ provided the proton conductors are in close proximity.

~~As can be seen, since~~ Since the proton conductors are bound, intercalated or included between the carbon skeletons, the proton conductor does not float. ~~Due to this~~ Therefore, even if the mixed conductor is used at  
15   a location where water is present, the proton conductor ~~[[does]] is not flow out~~ influenced by the water. That is, ~~a rate of lowering the~~ the loss of proton conduction ~~[[by]] in the presence of~~ water is very low.

~~Now, examples of the organic compound~~ Organic compounds having a  $\pi$  bond include unsaturated aliphatic ~~hydrocarbon~~ hydrocarbons and  
20   aromatic ~~hydrocarbon~~ hydrocarbons. More ~~concretely~~ preferably, at least one of polyacetylene, resorcinol, phenol, phenylphenol, polyaniline, polypyrrole, polythiophene, phenylphosphonic acid, and phenylsilane alkoxide ~~[[can be]] is~~ selected as a material for the organic compound having a  $\pi$  bond.

25           Further~~[[,]]~~ examples of the proton conducting material include ~~[[a]]~~ phosphorus-containing ~~compound~~ compounds, ~~[[a]]~~ sulfur-containing ~~compound~~ compounds, carbonic acid, boric acid, and inorganic solid-state

[[acid]] acids. ~~Examples~~ An example of the phosphorus-containing compound ~~include~~ is phosphoric acid and ~~principle~~ examples of the sulfur-containing compound include sulfuric acid and sulfonic acid. Further, an inorganic proton conducting material can be produced using a derivative of one of these compounds as a starting material. ~~In this case, particularly~~ Preferably, at least one of a phosphorus-containing compound, phosphoric acid, ~~ester phosphate~~ phosphate ester, sulfuric acid, ~~ester sulfate~~ sulfate ester, ~~sulfuric acid~~, tungsten oxide hydroxide, rhenium oxide hydroxide, silicon oxide, tin oxide, zirconia oxide, tungstophosphoric acid, and tungstosilicic acid ~~[[can be]]~~ is used.

To mineralize the organic compound in the precursor, it is preferable that the precursor ~~is burned under~~ be pyrolyzed in an inert atmosphere.

The inert atmosphere can be attained by putting the precursor ~~under the distribution~~ in an atmosphere of nitrogen gas or helium gas or in vacuum.

If the precursor is subjected to pyrolysis ~~[[under]]~~ in such an inert atmosphere, the organic component of the precursor is carbonized and thereby converted into an inorganic material. If the main chain of the organic component has a  $\pi$  bond, high electron conduction is ensured.

Heating temperature and heating time are appropriately selected according to the characteristics of the precursor.

Simultaneously with or after heating, ~~[[a]]~~ high energy ~~other than heat~~ radiation can be applied to the precursor. Examples of the high energy radiation include plasma radiation, microwave radiation and ultrasonic radiation.

As described above, the mixed conductor according to the present invention is made of inorganic materials and ~~exhibit~~ exhibits both an



electron conducting function and a proton conducting function. In addition, even in a low temperature range close to [[a]] room temperature, the mixed conductor functions properly. Further, even if water is present, the mixed conductor exhibits both electron conduction and proton conduction.

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## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a ~~typical view illustrating~~ schematic representation of the structure of a mixed conductor according to the present invention;

Fig. 2 is a ~~typical view illustrating~~ schematic representation of the structure of [[the]] another mixed conductor according to the present invention;

Fig. 3 is a ~~typical view illustrating~~ schematic representation of the structure of [[the]] yet another mixed conductor ~~in one embodiment~~ according to the present invention;

Fig. 4 is a ~~typical~~ schematic view of [[a holder]] an element for checking the proton conducting function of the mixed conductor [[in]] of the ~~embodiment~~ invention;

Fig. 5 is a chart showing the current-voltage characteristics of the ~~holder~~ element shown in Fig. 4; and

Fig. 6 is a chart showing the change [[of a]] in phosphoric acid ~~remaining rate~~ content with time in the mixed conductor immersed in pure water ~~in the embodiment~~.

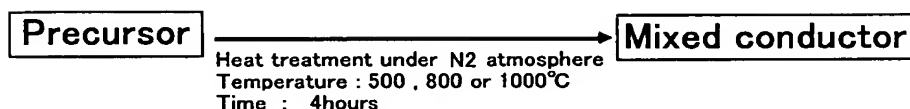
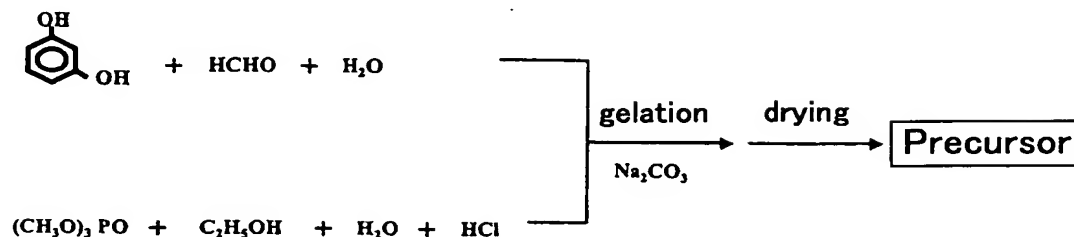
## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The above-stated advantages of the mixed conductor according to the present invention ~~will be~~ are confirmed hereinafter by way of exemplary ~~embodiments~~ by the examples which follow.

First, a method for producing a mixed conductor will be described

with reference to the following chemical formula 1, as well as Fig. 3.

### Chemical formula 1



5            Resorcinol (10 g) and formaldehyde (13 ml) are dissolved in water (40 ml), and a solution obtained by hydrolyzing trimethyl phosphate is added to the solution. The solution is then subjected to reflux at 100 to 200 for four hours and covalent ~~[[bond]]~~ bonding between electron conductor conductors and proton conductor conductors in the solution is promoted. The resultant solution is dehydrated and condensed with ~~Na<sub>2</sub>Co<sub>3</sub>~~ Na<sub>2</sub>CO<sub>3</sub> as a catalyst to gelate the solution. This gel is dried at 120°C, thereby obtaining a precursor.

15           This precursor is subjected to ~~[[a]]~~ pyrolysis (at 500 to 1000°C) under a nitrogen atmosphere to obtain a mixed conductor ~~in the embodiment.~~ This mixed conductor is constituted so that electronic wherein electron conductor phases 7 of a graphite-like structure and a proton conductor phase 9 containing phosphoric acid [[group]] groups are alternately aligned

as shown in Fig. 3.

The mixed conductor thus obtained is ground, pressed into a plate, ~~and put~~ placed between current collecting plates ~~to supply and supplied~~ with a DC current ~~to the plate formed mixed conductor~~. Specific resistance of each embodiment is obtained from a voltage at ~~that time~~. Measurement temperature is a room temperature.

10		<del>Embodiment</del>	<del>Embodiment</del>	<del>Embodiment</del>
		<u>Example 1</u>	<u>Example 2</u>	<u>Example 3</u>
	Heat treatment temperature	500°C	800°C	1000°C
	Specific resistance ( $\Omega$ cm)	138	0.35	0.13

~~In the embodiments, the reason of~~ The high specific resistance for the sample heat treated at a heating temperature of 500°C is considered to be due to insufficient carbonization of ~~[[an]]~~ the organic material.

The heating temperature and heating time are parameters that can be appropriately selected according to the structure and the like of the organic compound.

20        Next, a proton conduction test will be described with reference to Figs. 4 and 5.

As shown in Fig. 4, a backing layer 17 consisting of a carbon cloth and catalyst layer 15 is attached to each side of a sample 11 in each of ~~Embodiments~~ Examples 1 to 3. A Nafion membrane 13 transmits protons but blocks electrons.

25        A holder shown in Fig. ~~[[4is]]~~ 4 is put in a container, and nitrogen

gas or hydrogen gas at a temperature of 60°C and a relative humidity of 100% is introduced into the container. ~~[[A]]~~ The voltage-current characteristic at that time is shown in Fig. 5.

As can be seen from Fig. 5, even if a voltage is supplied between the backing layers 17 while introducing the nitrogen gas, no current is carried. On the other hand, if hydrogen gas is introduced into the container, it can be seen that a current flows. This demonstrates that the sample 11 has proton conduction.

Further, the proton conductivity of each sample is calculated as follows.

	<del>Embodiment</del> <u>Example 1</u>	<del>Embodiment</del> <u>Example 2</u>	<del>Embodiment</del> <u>Example 3</u>
Heat treatment temperature	500°C	800°C	1000°C
Proton conductivity (S/cm)	$2.6 \times 10^{-3}$	$1.3 \times 10^{-3}$	$7.3 \times 10^{-4}$

Further, as comparative examples, the proton conductivities of samples similarly subjected to a heat treatment by the ~~formation method in the embodiments already described above, but with omission of addition of and to which trimethyl phosphate, were~~ are not added are calculated as follows.

	<del>Comparative</del> Example 1	<del>Comparative</del> Example 2	<del>Comparative</del> Example 3
Heat treatment temperature	500°C	800°C	1000°C
Proton conductivity (S/cm)	$1.0 \times 10^{-6}$ or less	$1.0 \times 10^{-6}$ or less	$1.0 \times 10^{-6}$ or less

By ~~comparing~~ A comparison of the samples to which trimethyl phosphate ~~[[is]]~~ was added with those to which trimethyl phosphate ~~[[is]]~~ was not added, ~~the appearance of~~ confirms the proton conduction by phosphorus ~~is proven~~.

The relationship between immersion time and remaining phosphorus ~~remaining rate~~ content when samples (0.1 g) ~~[[in]]~~ of the respective ~~embodiments~~ examples are immersed in 1000 cc of pure water at ~~[[a]]~~ room temperature is shown in Fig. 6.

In Fig. 6, the phosphorus ~~remaining rate is~~ residual amount was measured by an EDX analyzer.

The result shown in Fig. 6 confirms that about 60% of phosphorus, about 80% of phosphorus, and about 90% of phosphorus (i.e., proton conduction) remains in the samples ~~in Embodiments of Examples~~ 1, 2, and 3, respectively~~[[.]]~~ , which

~~[[This]]~~ demonstrates that the mixed conductors ~~[[in]]~~ of the ~~embodiments keep~~ invention retain their proton conducting ~~functions~~ function even in a humid environment for a long time.

The mixed conductors can be used for fuel cells, and are particularly ~~suitably used for~~ suitable for use as the catalyst layers ~~constituting the~~ respective of fuel cells. The catalyst layer is at a location where oxygen or hydrogen supplied from the outside through the backing layers is ionized, and is normally arranged between the proton exchange membrane and the backing layer.

Examples of a method for producing a catalyst layer ~~[[if one]]~~ of the mixed conductors ~~is used as the catalyst layer~~ will next be described.

~~(Example 1)~~ Working Example 1

Each of the mixed conductors produced above is ground to powder by a ball mill or the like, and a platinum catalyst is supported on the mixed conductor thus ground ~~is caused to support a platinum catalyst~~. ~~The mixed conductor can be made to support the platinum catalyst~~ The platinum catalyst can be supported on the mixed conductor by the same method as ~~that for causing used to form a carbon holder in a process of forming a supported platinum carbon that constitutes catalyst used as the catalyst layer of an ordinary fuel cell to support a platinum catalyst~~. For example, chloroplatinic acid solution is impregnated with the mixed conductor powder and then subjected to a reducing treatment, ~~whereby~~ thereby forming the mixed conductor can support supported platinum catalyst.

The supporting mixed conductor is ~~mixed into~~ added to a Nafion solution, and mixed to produce a paste of ~~[[a]]~~ the mixture thereof is ~~produced~~, and this paste is screen-printed on each surface of an proton exchange membrane (a Nafion membrane in this example). As a result, a catalyst layer containing the mixed conductor is formed. Further, a backing layer is ~~connected~~ attached to the outside of the catalyst layer, whereby a unit of fuel cell ~~that constitutes the fuel cell~~, i.e., a unit cell, ~~[[can be]]~~ is produced.

## ~~(Example 2)~~ Working Example 2

Each of the mixed conductors produced above is ground to powder by a ball mill or the like, and a platinum catalyst is supported on the mixed conductor thus ground ~~is caused to support a platinum catalyst~~.

Next, the powder of the mixed conductor which supports the catalyst is subjected to hot pressing, thereby forming the mixed conductor into a shape corresponding to a target electrode to produce a catalyst layer. This catalyst layer is superposed on the proton exchange membrane and the

whole is ~~not press is conducted~~ pressed, whereby an integral formed article structure having the proton exchange membrane ~~[[put]]~~ between the catalyst layers is produced.

By ~~further connecting~~ attaching a backing layer to the outside of the catalyst layer, a unit cell of ~~[[the]]~~ a fuel cell ~~[[can be]]~~ is produced.

In the tests ~~stated~~ described above, the mixed conductors ~~[[in]]~~ of the examples exhibit both proton conduction and ~~electronic~~ electron conduction at a low temperature, in a range of ~~[[a]]~~ from room temperature to 60°C. Depending on the presence of water, ~~it is considered that~~ the mixed conductors exhibit ~~[[the]]~~ equivalent functions up to 200°C ~~under an~~ in the atmosphere.

It is seen that the mixed conductors ~~in the embodiments can~~ of the present invention exhibit their functions even at an extremely low temperature as compared with the conventional inorganic-based mixed conductor which exhibits its functions at a high temperature of about 800°C.

Furthermore, as is obvious from the structure shown in Fig.3, the ~~electronic~~ electron conductor phase 7 is connected to the proton conductor phase 9 by a covalent bond, so that they are quite proximate to each other. Due to this, even if a catalyst particle is very small, the electron conductor 7 and the proton conductor 9 ~~can be always~~ always be brought into contact with the catalyst particles simultaneously. This makes it possible to supply electrons and protons necessary for a catalytic reaction to the catalyst in proper quantities and thereby ~~improve~~ improves catalyst utilization efficiency.

The present invention is not limited ~~at all by the embodiments and by the above~~ description of the embodiments. The present invention also ~~contains~~ includes various changes and modifications thereto without

departure from the description of claims which follow, in a range that can be easily attained by a person having the ordinary level of skill in the art.





## Marked-Up Substitute Abstract

## ABSTRACT OF DISCLOSURE

[[A]] The mixed conductor of [[this]] the invention includes an electron conductor made of a carbon-based inorganic material ~~imparted electron conduction by causing~~ with a main chain ~~to have~~ having a  $\pi$  bond for conduction of electrons, and a proton conductor made of an inorganic material ~~having proton conduction~~, [[and]] wherein the electron conductor and the proton conductor are [[fixed]] attached to each other by ~~one of or all~~ at least one of [[a]] covalent [[bond]] bonding, intercalation, and inclusion.